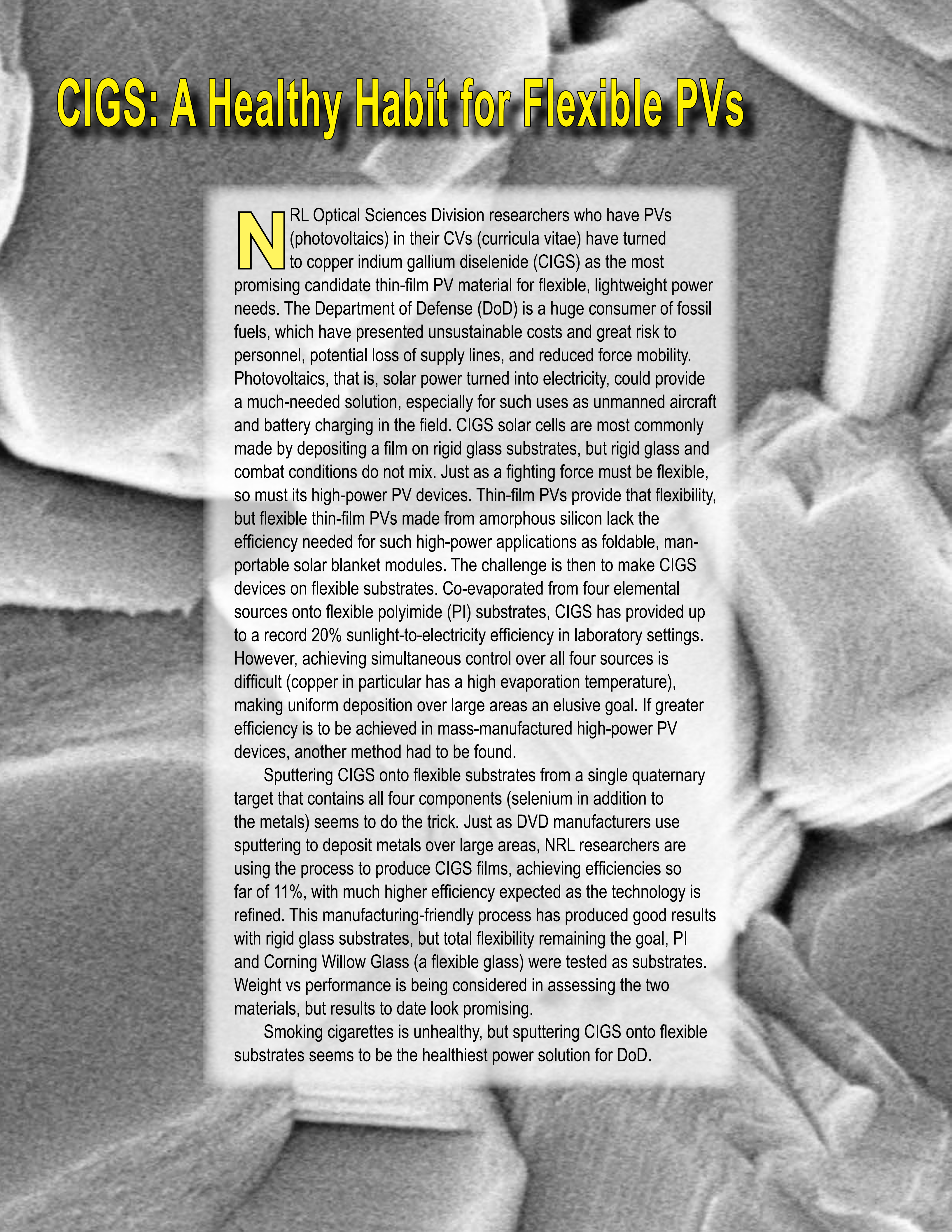


CIGS: A Healthy Habit for Flexible PVs

NRL Optical Sciences Division researchers who have PVs (photovoltaics) in their CVs (curricula vitae) have turned to copper indium gallium diselenide (CIGS) as the most promising candidate thin-film PV material for flexible, lightweight power needs. The Department of Defense (DoD) is a huge consumer of fossil fuels, which have presented unsustainable costs and great risk to personnel, potential loss of supply lines, and reduced force mobility. Photovoltaics, that is, solar power turned into electricity, could provide a much-needed solution, especially for such uses as unmanned aircraft and battery charging in the field. CIGS solar cells are most commonly made by depositing a film on rigid glass substrates, but rigid glass and combat conditions do not mix. Just as a fighting force must be flexible, so must its high-power PV devices. Thin-film PVs provide that flexibility, but flexible thin-film PVs made from amorphous silicon lack the efficiency needed for such high-power applications as foldable, man-portable solar blanket modules. The challenge is then to make CIGS devices on flexible substrates. Co-evaporated from four elemental sources onto flexible polyimide (PI) substrates, CIGS has provided up to a record 20% sunlight-to-electricity efficiency in laboratory settings. However, achieving simultaneous control over all four sources is difficult (copper in particular has a high evaporation temperature), making uniform deposition over large areas an elusive goal. If greater efficiency is to be achieved in mass-manufactured high-power PV devices, another method had to be found.

Sputtering CIGS onto flexible substrates from a single quaternary target that contains all four components (selenium in addition to the metals) seems to do the trick. Just as DVD manufacturers use sputtering to deposit metals over large areas, NRL researchers are using the process to produce CIGS films, achieving efficiencies so far of 11%, with much higher efficiency expected as the technology is refined. This manufacturing-friendly process has produced good results with rigid glass substrates, but total flexibility remaining the goal, PI and Corning Willow Glass (a flexible glass) were tested as substrates. Weight vs performance is being considered in assessing the two materials, but results to date look promising.

Smoking cigarettes is unhealthy, but sputtering CIGS onto flexible substrates seems to be the healthiest power solution for DoD.

Sputtered Thin-Film Absorbers for Flexible Photovoltaics

J.A. Frantz,[1] J.D. Myers,[1] R.Y. Bekele,[2] V.Q. Nguyen,[1] and J.S. Sanghera[1]
[1]*Optical Sciences Division*
[2]*University Research Foundation*

Flexible thin-film photovoltaics (PVs) have been proposed as an appealing power source for applications including unmanned aircraft systems and battery charging in the field. PVs based on silicon and III-V materials typically require thick substrates that add significant weight. Furthermore, their rigidity limits design options, requiring large, flat surfaces. Thin-film PVs offer a potential solution with specific power significantly higher than that of traditional PVs and the potential for flexible devices. Among thin-film PV materials, copper indium gallium diselenide (CIGS) has produced the best laboratory results on rigid glass substrates. Typically, CIGS is deposited by co-evaporation or, alternately, by deposition of the metals with, or followed by, treatment in a selenium environment. We present results from an alternative deposition method that instead uses sputtering from a single quaternary target. This technique is highly manufacturable, and we have already produced devices with conversion efficiencies of over 11%.

INTRODUCTION

The Department of Defense (DoD) is the world's largest organizational user of fossil fuels, with consumption of about 117 million barrels of oil in FY2011.[1] This heavy reliance on petroleum presents significant difficulties, including the vulnerability of supply lines to attack, reduced mobility of forces due to a dependence on supply lines, and loss of life in transporting fuel. The high cost of fuel is also a concern. A 2010 study by the Marine Corps in Afghanistan placed the fully burdened cost of fuel — a measure that includes the cost of personnel, equipment, and force protection required for transportation — at \$9 to \$16 per gallon if delivered by land and \$29 to \$31 for fuel delivered by air.[1] Furthermore, the need for electrical power frequently limits the lifetime and scope of missions for autonomous systems. Generation of some portion of the required electrical power in the field would relieve demands on the supply line, reduce the load carried by an individual soldier, and expand the capabilities of various unmanned platforms.

For these reasons, there has recently been intense interest in solar energy for DoD applications. Traditional PV materials, such as silicon and III-V material systems, are not ideally suited to all DoD needs since they use thick substrates that add significant weight and lack flexibility. Thin-film PVs offer the most promising potential solution, with specific power (measured in W/kg) significantly higher than that of traditional PVs and the potential for flexible devices such as a foldable solar blanket module that can be easily carried in a backpack.

First-generation flexible thin-film PV devices currently in use in the field are based on amorphous silicon PVs that typically provide 6% to 8% efficiency. A module with 20% efficiency would result in more than twice the power for the same size module. Existing thin-film PV technologies do not offer a viable pathway to achieving this efficiency since amorphous silicon PV is believed to be near its upper efficiency limit, and cadmium telluride must be deposited on a rigid glass substrate. PV devices based on copper indium gallium diselenide (CIGS), however, have been demonstrated on flexible polyimide (PI) and metal foil substrates. These materials present the most promising pathway to higher efficiency flexible modules.

The most well-established method of depositing CIGS is by co-evaporation from four independent elemental sources.[2] This technique has resulted in laboratory devices with record efficiencies of approximately 20%. While this method has produced excellent devices, there are several disadvantages associated with it. As a result of the point source nature of typical evaporation sources, uniform deposition over large areas is difficult. Copper, with the highest evaporation temperature, presents the greatest difficulty. Simultaneous control of all four sources can be challenging, with variations in relative deposition rate potentially leading to incorrect stoichiometry and diminished device performance.

QUATERNARY SPUTTERED CIGS

More recently, there has been interest in deposition by sputtering from a quaternary target — a single sputtering target that contains Se as well as the metals.[3] Sputtering is a well-established technology for large-area deposition. For instance, decorative window glass, the type one might see on an office building, is typically deposited by sputtering as are the coatings on rewritable DVDs. Naval Research Laboratory (NRL) scientists have developed a method that uses sputtering from a single quaternary target (i.e., one that contains all four constituent elements) without additional selenization. We have fabricated working devices using CIGS films that are sputtered in a single step and have demonstrated conversion efficiency as high as 11%. This technique offers the potential for scale-up to large volume manufacturing on flexible substrates.

Figure 1 illustrates the quaternary sputtering process developed at NRL. Bulk CIGS is formed by heating high purity precursors in a vacuum-sealed quartz ampoule. The bulk material is ground into a powder inside a nitrogen-purged glovebox, and sputtering targets are formed by hot-pressing the powder into 3 in. diameter disks. The disks are then machined to the proper dimensions and indium-bonded to a copper backing plate. The targets are installed in a sputter deposition system, and 2 μm thick CIGS films are deposited at an elevated temperature of 550 °C onto substrates that were previously coated with a sputtered Mo bottom contact. Figure 2 is a schematic diagram of the structure of a typical CIGS cell. After the p-type CIGS material is deposited, a 50 nm thick layer of n-type CdS is deposited in order to form a junction. Several hundred nanometers of ZnO and Al_2O_3:ZnO (AZO) are deposited by sputtering to serve as a transparent top contact. Finally, patterned grids composed of Ni and Al, which aid in charge collection, are deposited via evaporation. The vacuum deposition steps are performed in a cluster tool in the Optical Sciences Division as shown in Fig. 3. This system includes a glove box, two sputterers (one of which is designed especially for selenium- and sulfur-based compounds), and two evaporators. The system allows a different deposition mask to be applied for each layer, permitting the fabrication of complex, multilayer devices without ever removing samples to air.

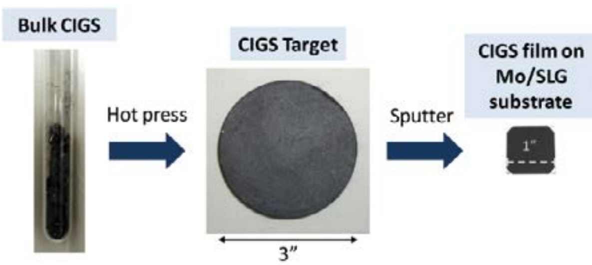


FIGURE 1
Fabrication steps in a quaternary sputtered CIGS process. Bulk material is batched, pressed into a disk, and machined to appropriate dimensions for a target. Thin films are sputtered under high vacuum. SLG = soda lime glass.

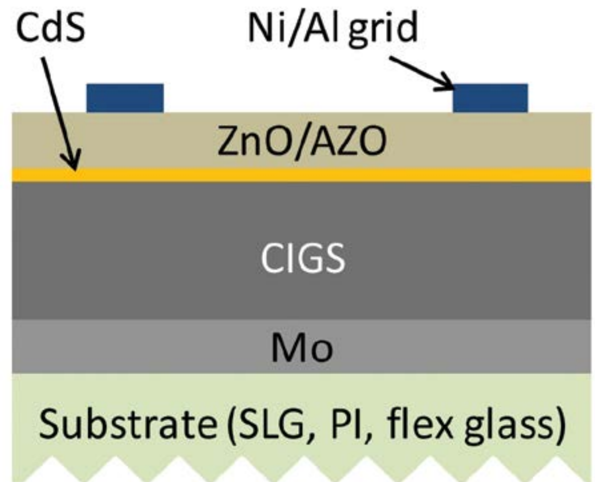


FIGURE 2
Schematic diagram of a typical CIGS cell.

FIGURE 3
Vacuum deposition cluster tool in the Optical Sciences Division. A glove box allows sample loading and manipulation without exposure to air, and robotic transfer moves samples among chambers to build complex, multilayer devices.

SEM images, shown in Fig. 4, compare the structure of an evaporated film, fabricated externally to NRL, with a quaternary sputtered film. Both deposition methods yield dense films, with 1 μm scale grains at the top surface. One significant difference is the presence in the sputtered film of ~100 nm scale grains near the Mo/CIGS interface that coalesce into larger grains near the top surface of the film.

Figure 5 shows device results from a typical 0.5 cm^2 sputtered CIGS device. Light *J–V* curves were obtained in a solar simulator under one sun, AM1.5G illumination, conditions meant to simulate unconcentrated sunlight on Earth's surface. For this device, the short circuit current density is 34 mA/cm^2, the open circuit voltage is 490 mV, the fill factor is 64%, and the sunlight to electricity conversion efficiency is 11%. The inset plot shows the external quantum efficiency (EQE), a measure of the incident photons that produce charge carriers, as a function of wavelength. The EQE is above 80% for short wavelengths, consistent with high-quality absorber material.

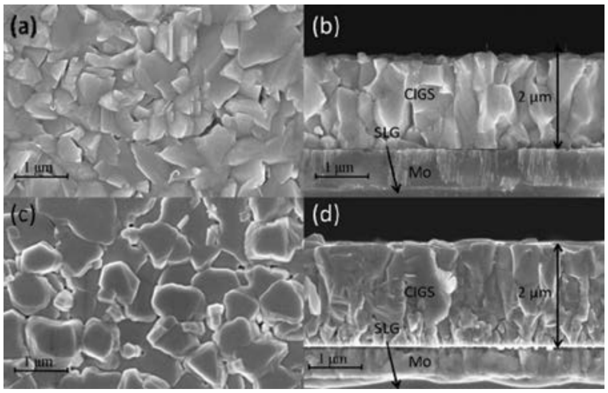


FIGURE 4
SEM images showing a top view (a) and cross section (b) of evaporated CIGS and a top view (c) and cross section (d) of sputtered CIGS.

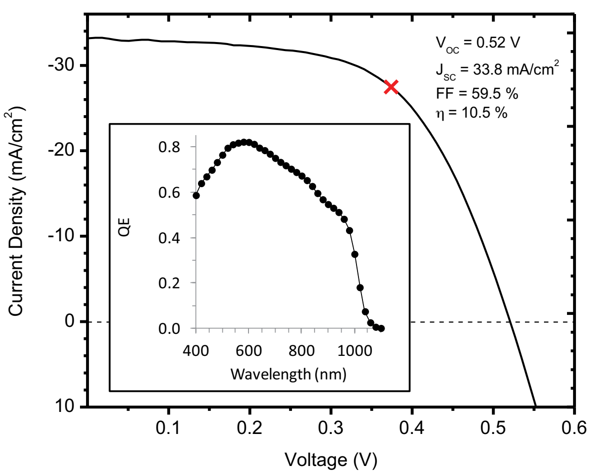


FIGURE 5
Light *J–V* of a sputtered CIGS device measured under AM1.5 illumination. The red "X" indicates the point of maximum power, and the inset shows measured EQE.

MANUFACTURABILITY AND SCALE-UP

To make a large impact on energy consumption for DoD applications, large areas of PV materials will be needed. Sputtering is a technology that is well suited for scale-up to an industrial process. One factor that is important in this case is material utilization. During sputtering, material is preferentially removed from the target in a characteristic "racetrack" pattern, based on the distribution of the magnetic field. Typically, about 50% of the material is used before the entire thickness of the target is consumed within a racetrack. In order to assure that unused material can be reclaimed, we performed a series of experiments in which several old targets were recycled into new ones. Figure 6(a) shows a spent target with a characteristic racetrack pattern, while Fig. 6(b) shows a target made of reclaimed material. The performance of the resulting devices was as good as the performance of those made from unused precursors, demonstrating material utilization for the quaternary sputtering process can be very high.

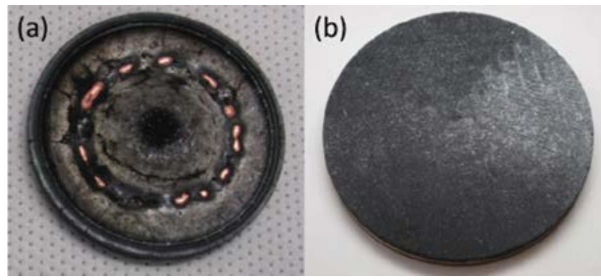


FIGURE 6
A spent target is shown in (a), with a typical racetrack wear pattern visible, while (b) shows a target formed from material recaptured from two spent sputtering targets.

SPUTTERED CIGS ON FLEXIBLE SUBSTRATES

Results for sputtered films on rigid glass substrates have been promising, indicating that the method is viable for scale-up for manufacturing purposes. The ultimate goal, however, is a large-scale process that can be used to make flexible solar cells. Two flexible substrate materials, polyimide and Corning Willow Glass, were evaluated for this purpose. Willow Glass is a flexible glass with a bending radius small enough that it is compatible with roll-to-roll processing. Calculations of module weight were made assuming a module efficiency of 15% for each substrate type, unconcentrated AM1.5G illumination, and substrate thicknesses of 1 mm for the soda lime glass (SLG) and 50 µm for each of the thin-film materials.

The weight of each of the thin-film substrates is significantly less than that of the rigid glass substrate, with PI lighter by a factor of more than 30, and Willow Glass lighter by a factor of more than 20. Willow Glass has the advantage that it can withstand temperatures above 600 °C, making it compatible with the high temperatures preferred in CIGS processing. Devices on polyimide, on the other hand, must be deposited below the optimum deposition temperature of 550 °C to prevent degrading the PI. Even though Willow Glass is slightly heavier than PI, the higher processing temperatures may eventually result in better device performance, so NRL is continuing to assess both materials.

To evaluate NRL's technology for use with flexible substrates, the sputtered CIGS process was applied to make devices on several types of flexible substrates. CIGS was sputtered onto 125 μm thick PI films and onto 100 μm thick sheets of Willow Glass. Figure 7 shows several examples of working flexible sputtered CIGS devices. Figure 7(a) shows devices on a PI substrate. A Willow Glass substrate with a 3 × 3 array of Mo bottom contacts is shown in Fig. 7(b). The inset shows completed devices on one of the bottom contact pads. A polymer protection tab, visible as an orange band in the images, was used for handling during fabrication.

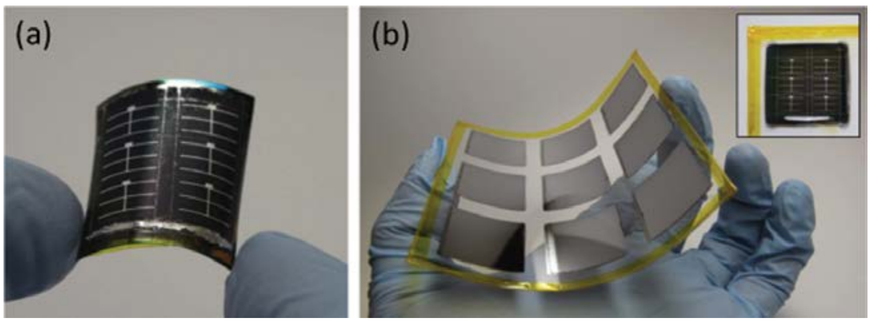


FIGURE 7
Flexible substrates for sputtered CIGS. A PI substrate with completed devices is shown in (a). A Corning Willow Glass substrate with a 3x3 array of Mo bottom contacts is shown in (b). The inset shows completed devices on one of the bottom contact pads.

CONCLUSIONS

Quaternary sputtered CIGS offers a promising pathway to the large-scale manufacturing of flexible thin-film solar cells. Sputtering is a well-established technique for large-scale manufacturing, and NRL's work has demonstrated that it is viable for CIGS-based PVs. With target reclamation, material utilization is quite high, making the technology cost effective as well. The method has been demonstrated to produce working devices on several types of flexible substrates. Moving forward, this technology is viable for scale-up for large-area, roll-to-roll deposition, and has a promising future for DoD applications such as power for unmanned aircraft systems and battery charging in the field.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Office of Naval Research and Sunlight Photonics, Inc. They also thank their collaborators in the Solid State Devices Branch: Dr. Sergey Maximenko, who obtained the EQE data, Dr. Maria Gonzalez, Dr. Joe Tischler, and Dr. Robert Walters.

[Sponsored by the NRL Base Program (CNR funded) and Sunlight Photonics, Inc.]

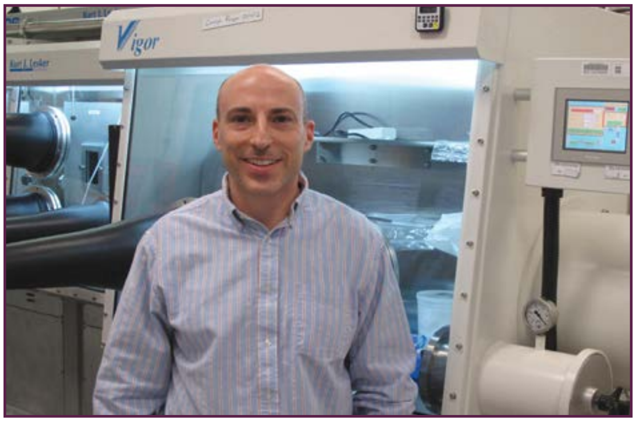
References

[1] M. Schwartz, K. Blakeley, and R. O'Rourke, "Department of Defense Energy Initiatives: Background and Issues for Congress," Congressional Research Service, Dec. 10, 2012.

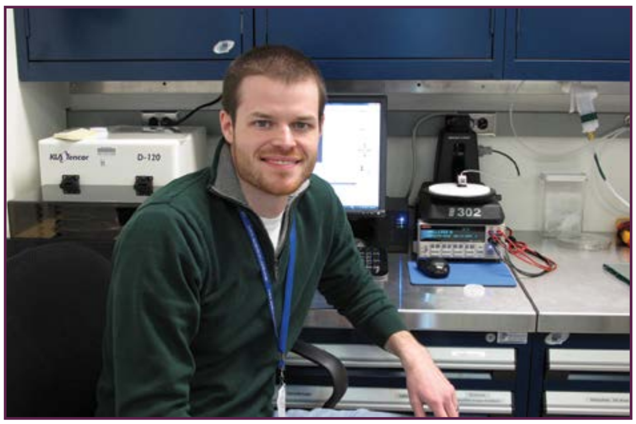
[2] S. Niki, M. Contreras, I. Repins, M. Powalla, K. Kushiya, S. Ishizuka, and K. Matsubara, "CIGS Absorbers and Processes," *Prog. Photovolt. Res. Appl.* **18**, 453–466 (2010).

[3] J.A. Frantz, R.Y. Bekele, V.Q. Nguyen, J.S. Sanghera, A. Bruce, S.V. Frolov, M. Cyrus, and I.D. Aggarwal, "Cu(In,Ga)Se_2 Thin Films and Devices Sputtered from a Single Target without Additional Selenization," *Thin Solid Films* **519**, 7763–7765 (2011).

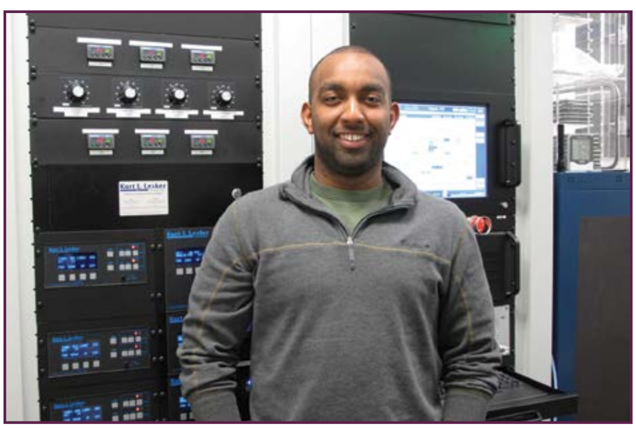
THE AUTHORS



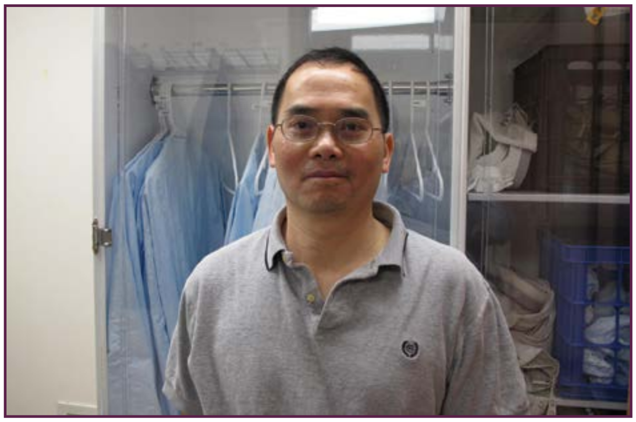
JESSE FRANTZ has been a physicist at NRL since 2004 where his research is focused on the development of novel thin-film materials and scalable processing techniques. He studies selenide- and sulfide-based films for applications including flexible photovoltaics and infrared planar waveguides. He helped establish a new vacuum deposition cluster system facility, the Laboratory for Research in Integrated and Advanced Thin Films — a major capital equipment facility in NRL's Optical Sciences Division that is being used for a variety of projects, including the fabrication of advanced, multilayer thin films for photovoltaic applications. He received his Ph.D. in optical sciences from the University of Arizona in 2004, an M.S. in optical sciences from the University of Arizona in 1999, and a B.A. in physics from Vassar College in 1997.



JASON D. MYERS joined NRL as a Karles Fellow in 2011. Since then, his work has focused on chalcogenide photovoltaic materials, novel device processing, and advanced thin-film deposition techniques. Dr. Myers graduated in 2011 with his doctoral degree in materials science and engineering from the University of Florida in Gainesville, specializing in organic-based photovoltaic devices. His research interests include characterization and deposition of thin-film materials, photovoltaic device physics, and novel photovoltaic materials.



ROBEL BEKELE received his B.S. in physics and economics from Vanderbilt University in 2007 and his M.S. in materials science and engineering from the University of Florida in 2009. At Florida, he worked on unique fabrication methods for photovoltaic (PV) devices, including soft lithography and oblique angle deposition. Since 2009, he has worked at NRL on thin-film PVs. In his time at NRL, he has worked on developing techniques for manufacturing $Cu(InGa)Se_2$ sputtering targets and using those targets to deposit films for PV devices. His research interests include organic and inorganic photovoltaic materials, semiconductor device physics, and advanced fabrication techniques.



VINH NGUYEN has worked at NRL since 1992 as a material engineer. His main research interests include the development of chemical purification techniques and processes to make low-loss infrared transmitting chalcogenide optical fibers and high purity Cu-In-Ga-Se polycrystalline materials to be used for making thin films for photovoltaic applications. He received his Ph.D. in materials science and engineering (MS&E) from the University of Maryland, College Park, in 1999, an M.S. in MS&E from the University of California, Los Angeles, in 1992, and a B.S. in mechanical engineering from the University of California, Irvine, in 1990.

JAS SANGHERA is head of the Optical Materials and Devices Branch at NRL, where he manages and technically guides about 30 scientists in all aspects of optical materials research. The branch is involved with the research and development of novel glasses, crystals, and ceramics with superior properties that can be leveraged for enhancing the performance of existing applications or enabling new applications.